



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G03F 7/00, B41M 3/00	A1	(11) International Publication Number: WO 98/10334 (43) International Publication Date: 12 March 1998 (12.03.98)
(21) International Application Number: PCT/US97/15566 (22) International Filing Date: 4 September 1997 (04.09.97) (30) Priority Data: 08/707,456 4 September 1996 (04.09.96) US (71) Applicant: KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 North Lake Street, Neenah, WI 54956 (US). (72) Inventor: EVERHART, Dennis, Stein; 230 Hereford Road, Alpharetta, GA 30201 (US). (74) Agents: HARPS, Joseph, P. et al.; Kimberly-Clark Worldwide, Inc., 401 North Lake Street, Neenah, WI 54956 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: METHOD OF CONTACT PRINTING ON METAL ALLOY-COATED POLYMER FILMS		
(57) Abstract <p>The present invention comprises methods of contact printing of patterned, self-assembling monolayers of alkanethiolates, carboxylic acids, hydroxamic acids, and phosphonic acids on thermoplastic films metallized with an alloy such as nickel/gold, the compositions produced thereby, and the use of these compositions. Patterned self-assembling monolayers allow for the controlled placement of fluids thereon which contain a chemically reactive, indicator functionality. The optical sensing devices produced thereby when the film is exposed to an analyte and light, can produce optical diffraction patterns which differ depending on the reaction of the self-assembling monolayer with the analyte of interest. The light can be in the visible spectrum, and be either reflected from the film, or transmitted through it, and the analyte can be any compound reacting with the fluid on the self-assembling monolayer. The present invention also provides a flexible support for a self-assembling monolayer on a metal alloy.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD OF CONTACT PRINTING ON METAL ALLOY-COATED POLYMER FILMS

Technical Field

The present invention is in the field of contact printing and, more specifically the present invention is in the field of microcontact printing on polymer films.

Background of the Invention

Microcontact printing is a technique for forming patterns of organic monolayers with μm and submicron lateral dimensions. It offers experimental simplicity and flexibility in forming certain types of patterns. It relies on the remarkable ability of self-assembled monolayers of long-chain alkanethiolates to form on gold and other metals. These patterns can act as nanometer resists by protecting the supporting metal from corrosion by appropriately formulated etchants, or, can allow for the selective placement of fluids on hydrophilic regions of the pattern. Patterns of self-assembled monolayers having dimensions that can be less than $1\ \mu\text{m}$ are formed by using the alkanethiol as an "ink", and by printing them on the metal support using an elastomeric "stamp". The stamp is fabricated by molding a silicone elastomer using a master prepared by optical or X-ray microlithography or by other techniques.

Microcontact printing of patterned self-assembled monolayers brings to microfabrication a number of new capabilities. First, microcontact printing makes it possible to form patterns that are distinguished only by their constituent functional groups; this capability permits the control of surface properties such as interfacial free energies with great precision. Second, because micro-contact printing relies on molecular self-assembly, it generates a system that is (at least locally) close to a thermodynamic minimum and is intrinsically defect-rejecting and self-healing. Simple procedures, with minimal protection against surface contamination by adsorbed materials or by particles, can lead to surprisingly low levels of defects in the final structures. The procedure can be conducted at atmospheric pressure, in an unprotected laboratory atmosphere. Thus, microcontact printing is especially useful in laboratories that do not have routine access to the equipment normally used in microfabrication, or for which the capital cost of equipment is a serious concern. Third, the patterned self-

assembled monolayers can be designed to act as resists with a number of wet-chemical etchants.

Working with liquid etchants suffers from the disadvantages of handling solvents and disposing of wastes, but also enjoys substantial advantages: a high degree of control over contamination of surfaces; reduced damage to the substrate from energetic interactions with atoms or ions; the ability to manipulate complex and sensitive organic functionality. Because the self-assembled monolayers are only 1 - 3 nm thick, there is little loss in edge definition due to the thickness of the resist; the major determinants of edge resolution seem to be the fidelity of the contact printing and the anisotropy of etching the underlying metal. In the current best cases, features of size 0.2 μm can be fabricated; edge resolution in systems showing this resolution in feature size is less than 50 nm.

In the prior art, a gold film 5 to 2000 nanometers thick is typically supported on a titanium-primed Si/SiO₂ wafer or glass sheet. The titanium serves as an adhesion promoter between gold and the support. However, the silicon wafer is rigid, brittle, and cannot transmit light. These silicon wafers are also not suitable for a large-scale, continuous printing process, such as in letterpress, gravure, offset, and screen printing (see Printing Fundamentals, A. Glassman, Ed. (Tappi Press Atlanta, GA 1981); Encyclopedia Britannica, vol. 26, pp. 76-92, 110-111 (Encyclopedia Britannica, Inc. 1991)). In addition, silicon must be treated in a separate step with an adhesion promoter such as Cr or Ti, or Au will not adequately adhere, preventing formation of a stable and well-ordered self-assembling monolayer. Finally, silicon is opaque, so any diffraction pattern obtained must be created with reflected, not transmitted light. What is needed is an easy, efficient and simple method of contact printing on an optically transparent, flexible substrate, that is amenable to continuous processing.

Summary of the Invention

The present invention comprises methods of contact printing of patterned, self-assembling monolayers of alkanethiolates, carboxylic acids, hydroxamic acids, and phosphonic acids on thermoplastic films metallized with an alloy such as nickel/gold, the compositions produced thereby, and the use of these compositions.

Patterned self-assembling monolayers allow for the controlled placement of fluids thereon which can contain a chemically reactive, indicator functionality. The optical sensing devices produced thereby when the film is exposed to an analyte and light, can produce optical diffraction patterns which differ depending on the reaction of the self-assembling monolayer with the analyte of interest. The light can be in the visible spectrum, and be either reflected from the film, or transmitted through it, and the analyte can be any compound reacting with the self-assembling monolayer. The present invention also provides a flexible support for a self-assembling monolayer on a metal alloy.

The present invention includes a support for a self-assembling monolayer on a metal alloy which does not require an adhesion promoter for the formation of a well-ordered self-assembling monolayer. The present invention also provides a support for a self-assembling monolayer on a metal alloy which is suitable for continuous, rather than batch, fabrication. Finally the present invention provides a low-cost, disposable sensor which can be mass produced.

These and other objects, features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments.

Brief Description of the Figures

Figure 1 is a schematic of contact printing of self-assembling monolayers, using a nickel/gold coated polymer substrate as an example. A polydimethylsiloxane (PDMS; silicone elastomer 184; Dow Corning Corp., Midland, MI) is polymerized on a silicone master containing a pre-determined pattern. The PDMS is peeled away from the master, and then exposed to a solution containing $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. The alkane-thiol coated stamp is then stamped onto the nickel/gold-coated substrate. Then, the surface of the substrate is exposed to a solution containing a different alkane thiol such as $\text{HS}(\text{CH}_2)_{11}\text{OH}$.

Figure 2 is a field emission secondary electron microscope image of 10 micron-diameter circles of hydrophilic self-assembling monolayers formed by printing of 16-mercaptohexadecanoic acid onto MYLAR® metallized with Ni/Au alloy, as described in Example 1.

Figure 3a is an optical photomicrograph at 300x magnification of 10 micron-diameter circles of hydrophilic self-assembling monolayers formed by printing of 16-mercaptohexadecanoic acid, as described in Example 1, below, and after exposure to a high surface energy, curable, optical adhesive. The adhesive was cured by ultraviolet light (UV) exposure.

Figure 3b is a photograph of the diffraction pattern formed by visible light shown through the self-assembling monolayer pattern described by Figure 3a.

Figures 4a and 4b are a field emission secondary electron micrograph image of 10 micron-diameter circles formed of self-assembled photocurable polymers on hydrophilic self-assembling monolayers, printed as described in Example 1.

Detailed Description

The present invention provides methods of contact printing of patterned, self-assembling monolayers of alkanethiolates, carboxylic acids, hydroxamic acids, and phosphonic acids on polymer films metallized with an alloy such as nickel/gold, desirably thermoplastic polymer films, the compositions produced thereby, and the use of these compositions. Patterned self-assembling monolayers allow for the controlled placement of fluids thereon which can contain a chemically reactive, indicator functionality. The term "patterned self-assembling monolayers thereon" as used herein means the self-assembling monolayers in any pattern on the metallized polymer films including a solid pattern.

In one embodiment, optical sensing devices can be produced according to the present invention. When the film with the self-assembling monolayers thereon is exposed to an analyte that is capable of reacting with the self-assembling monolayer, the film will produce optical diffraction patterns which differ depending on the reaction of the self-assembling monolayer with the analyte of interest. The liquid may be a high surface tension fluid such as water. The light can be in the visible spectrum, and be either reflected from the film, or transmitted through it, and the analyte can be any compound reacting with the self-assembling monolayer.

Self-assembled monolayers of organic compounds on inorganic or metal surfaces are becoming increasingly important in many areas of materials science. Although there are many different systems of self-assembling monolayers based on different organic

components and supports, desired systems are those of alkanethiolates, $\text{HS}(\text{CH}_2)_n\text{R}$. Typically, a gold film, 5 to 2000 nm thick, is supported on a titanium-primed Si/SiO₂ wafer or glass sheet. The titanium serves as an adhesion promoter between gold and the support. The alkanethiols chemisorb on the gold surface from a solution in which the gold film is immersed, and form adsorbed alkanethiolates with loss of hydrogen. Adsorption can also occur from the vapor. Self-assembling monolayers formed on gold from long-chain alkanethiolates of structure $\text{X}(\text{CH}_2)_n\text{Y}(\text{CH}_2)_m\text{S}$ are highly ordered and can be considered as crystalline or quasi-crystalline molecular arrays. A wide variety of organic functional groups (X,Y) can be incorporated into the surface or interior of the monolayer.

Self-assembling monolayers can therefore be tailored to provide a wide variety of material properties: wettability and protection against corrosion by chemical etchants are especially relevant to μCP . In one embodiment of the invention, there are two or more self-assembling monolayers with different chemical properties. In another embodiment of the invention, a first self-assembling monolayer is hydrophobic, and a second self-assembling monolayer is hydrophilic.

Figure 1 outlines the procedure used for microcontact printing. An elastomeric stamp is used to transfer by contact alkanethiol "ink" to a surface coated with a metal alloy. In a preferred embodiment, the alloy surface is predominantly gold. Preferred alloys are those such as nickel/gold, which are known to show an enrichment in the surface concentration of gold relative to its bulk concentration. Prediction of surface segregation of one metal of an alloy is described in M.P. Seah, "Quantitative Prediction of Surface Segregation," Journal of Catalysis, vol. 57, pp. 450-457 (1979), and J.J. Burton, *et al.*, "Prediction of Segregation to Alloy Surfaces from Bulk Phase Diagrams," Physical Review Letters, vol. 37, No. 21, pp. 1433-1436 (Nov. 22, 1976), both incorporated herein by reference. In one embodiment of the invention, the metal alloy has surface enrichment of a metal reacting with the self-assembling monolayer. If the stamp is patterned, a patterned self-assembling monolayer forms. The stamp is fabricated by casting polydimethylsiloxane (PDMS) on a master having the desired pattern. Masters are prepared using standard photolithographic techniques, or constructed from existing materials having microscale surface features.

In a typical experimental procedure, a photolithographically produced master is placed in a glass or plastic Petri dish, and a 10:1 ratio (w:w or v:v) mixture of SYLGARD silicone elastomer 184 and SYLGARD silicone elastomer 184 curing agent (Dow Corning Corporation) is poured over it. The elastomer is allowed to sit for approximately 30 minutes at room temperature and pressure to degas, then cured for 1 - 2 hours at 60°C, and gently peeled from the master. "Inking" of the elastomeric stamp is accomplished by exposing the stamp to a 0.1 to 1.0 mM solution of alkanethiol in anhydrous ethanol, either by pouring the solution over the surface of the stamp, or by rubbing the stamp gently with a Q-tip that has been saturated with the inking solution. The stamp is allowed to dry until no liquid is visible by eye on the surface of the stamp (typically about 60 seconds), either under ambient conditions, or by exposure to a stream of nitrogen gas. Following inking, the stamp is applied (typically by hand) to a metal alloy, *e.g.*, nickel/gold surface. Very light hand pressure is used to aid in complete contact between the stamp and the surface. The stamp is then gently peeled from the surface. Following removal of the stamp, the surface is washed of excess thiol and the patterned metal alloy surface can be subjected to chemical etchants (see below) that selectively remove underivatized areas of the metal alloy surface, and if desired, the underlying support(s). Alternatively, further derivatization of unstamped areas can be accomplished, either by using a second stamp, or by washing the entire surface with a different alkanethiol.

The elastomeric character of the stamp is essential to the success of the process. Polydimethylsiloxane (PDMS), when cured, is sufficiently elastomeric to allow good conformal contact of the stamp and the surface, even for surfaces with significant relief; this contact is essential for efficient contact transfer of the alkanethiol "ink" to the alloy-coated film. The elastomeric properties of PDMS are also important when the stamp is removed from the master: if the stamp were rigid (as is the master) it would be difficult to separate the stamp and master after curing without damaging one of the two substrates. PDMS is also sufficiently rigid to retain its shape, even for features with sub-micron dimensions: we have successfully generated patterns with lines as small as 200 nm in width. The surface of PDMS has a low interfacial free energy ($\gamma = 22.1$ dynes/cm), and the stamp does not adhere to the metal alloy coated film. The stamp is durable: we have used the same stamp up to 100 times over a period of several months

without significant degradation in performance. The polymeric nature of PDMS also plays a critical role in the inking procedure, by enabling the stamp to absorb the alkanethiol ink by swelling.

Microcontact printing on metal alloy surfaces can be conducted with a variety of alkanethiol "inks". Alkanethiols that do not undergo reactive spreading (after application to the metal alloy film) are required for formation of small features with high resolution. For stamping in air, one can use autophobic alkanethiols such as hexadecanethiol. Microcontact printing of other non-autophobic alkanethiols, for example, $\text{HS}(\text{CH}_2)_{15}\text{COOH}$, can be conducted by stamping under a liquid such as water. Patterned self-assembling monolayers of alkanethiols on metal alloy provide excellent resist character with a number of wet-chemical etchants.

In one embodiment of the present invention, the self-assembling monolayer is formed of a carboxy-terminated alkane thiol stamped with a patterned elastomeric stamp onto a nickel/gold-surfaced thermoplastic film such as MYLAR[®]. The alkanethiol is inked with a solution of alkanethiol in ethanol, dried, and brought into contact with a surface of nickel/gold. The alkanethiol is transferred to the surface only at those regions where the stamp contacts the surface, producing a pattern of self-assembling monolayer which is defined by the pattern of the stamp. Optionally, areas of unmodified nickel/gold surface next to the stamped areas can be rendered hydrophobic by reaction with a methyl-terminated alkane thiol.

A more detailed description of the methods and compositions of the present invention follows. All publications cited herein are incorporated by reference in their entirety.

Any thermoplastic film upon which a metal substrate can be deposited is suitable for the present invention. These include, but are not limited to polymers such as: polyethylene-terephthalate (MYLAR[®]), acrylonitrile-butadiene-styrene, acrylonitrile-methyl acrylate copolymer, cellophane, cellulosic polymers such as ethyl cellulose, cellulose acetate, cellulose acetate butyrate, cellulose propionate, cellulose triacetate, cellulose triacetate, polyethylene, polyethylene - vinyl acetate copolymers, ionomers (ethylene polymers) polyethylene-nylon copolymers, polypropylene, methyl pentene polymers, polyvinyl fluoride, and aromatic polysulfones. Preferably, the plastic film has an optical transparency of greater than 80%. Other suitable thermoplastics and suppliers

may be found, for example, in reference works such as the *Modern Plastics Encyclopedia* (McGraw-Hill Publishing Co., New York 1923-1996).

In one embodiment of the invention, the thermoplastic film with the metal coating thereon has an optical transparency of between approximately 5% and 95%. A more desired optical transparency for the thermoplastic film used in the present invention is between approximately 20% and 80%. In a desired embodiment of the present invention, the thermoplastic film has at least an approximately 80% optical transparency, and the thickness of the metal coating is such as to maintain an optical transparency greater than about 20%, so that diffraction patterns can be produced by either reflected or transmitted light. This corresponds to a metal coating thickness of about 20 nm. However, in other embodiments of the invention, the gold thickness may be between approximately 1 nm and 1000 nm.

The preferred metal alloy for deposition on the film is gold and another metal. However, alloys of silver, aluminum, copper, iron, zirconium, platinum, nickel may also be used. Preferred metals are ones that do not form oxides, and thus assist in the formation of more predictable self-assembling monolayers. Alloys such as Ni/Au, Pt/Au, and Cu/Au, which show surface enrichments of Au, are suitable.

In principle, any surface with corrugations of appropriate size could be used as masters. The process of microcontact printing starts with an appropriate relief structure, from which an elastomeric stamp is cast. This 'master' template may be generated photolithographically, or by other procedures, such as commercially available diffraction gratings. In one embodiment, the stamp may be made from polydimethylsiloxane.

In one embodiment of the present invention, the self-assembling monolayer has the following general formula:



X is reactive with metal or metal oxide. For example, X may be asymmetrical or symmetrical disulfide (-R'SSR, -RSSR), sulfide (-R'SR, -RSR), diselenide (-R'Se-SeR), selenide (-R'SeR, -RSeR), thiol (-SH), nitrile (-CN), isonitrile, nitro (-NO₂), selenol (-SeH), trivalent phosphorous compounds, isothiocyanate, xanthate, thiocarbamate,

phosphine, thioacid or dithioacid, carboxylic acids, hydroxylic acids, and hydroxamic acids.

R and R' are hydrocarbon chains which may optionally be interrupted by hetero atoms and which are preferably non-branched for the sake of optimum dense packing. At room temperature, R is greater than or equal to seven carbon atoms in length, in order to overcome natural randomizing of the self-assembling monolayer. At colder temperatures, R may be shorter. In a preferred embodiment, R is $-(CH_2)_n-$ where n is between 10 and 12, inclusive. The carbon chain may optionally be perfluorinated.

Y may also have any surface property of interest. For example, Y could be any among the great number of groups used for immobilization in liquid chromatography techniques, such as hydroxy, carboxyl, amino, aldehyde, hydrazide, carbonyl, epoxy, or vinyl groups. Examples of sensing layer materials are set forth in "Patterning Self-Assembled Monolayers Using Microcontact Printing: A New Technology for Biosensors?," by Milan Mrksich and George M. Whitesides, published in TIBTECH, June, 1995 (Vol. 13), pp. 228-235, hereby incorporated by reference.

Self-assembling monolayers of alkyl phosphonic, hydroxamic, and carboxylic acids may also be useful for the methods and compositions of the present invention. Since alkanethiols do not adsorb to the surfaces of many metal oxides, carboxylic acids, phosphonic acids, and hydroxamic acids may be preferred for X for those metal oxides. See J. P. Folkers, G.M. Whitesides, *et al.*, *Langmuir*, 1995, vol. 11, pp. 813-824.

R may also be of the form $(CH_2)_a-Z-(CH_2)_b$, where $a \geq 0$, $b \geq 7$, and Z is any chemical functionality or compound of interest, such as sulfones, urea, lactam, etc.

The stamp may be applied in air, or under a fluid such as water to prevent excess diffusion of the alkanethiol. For large-scale or continuous printing processes, it is most desirable to print in air, since shorter contact times are desirable for those processes.

In one embodiment of the present invention, the pattern is formed on the metallized thermoplastic polymer with the self-assembling monolayer. In another embodiment of the present invention, the relief of the pattern is formed with the self-assembling monolayer. After the stamping process, the metallized areas on the plastic may optionally be passivated, for example, with a methyl-terminated self-assembling monolayer such as hexadecylmercaptan.

This invention is further illustrated by the following example, which is not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof, which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention.

Example 1

Printing of nickel/gold-coated MYLAR® (polyethylene terephthalate) with patterns of 16-mercaptohexadecanoic acid and hexadecanethiol

A nickel/gold alloy was sputter-coated onto 7 mil MYLAR® of 15.9 nM thickness. The composition had 65% visible light transmittance, and 65 ohms/cm² resistance. The following results from XPS surface analysis were obtained.

Sputter Time (sec)	%C	%O	%Au	%Ni
0	51.5	8.0	40.5	ND
15	33.3	6.4	60.3	ND
30	20.2	ND	71.7	8.0
60	19.3	ND	72.4	8.3

ND means "not detected", i.e., less than 0.2 atom-percent.

These results show that the outermost surface of the Ni/Au alloy is predominantly Au, i.e., Ni is not detected until after approximately 5.0 nM of Au is removed. Thus, the alloy presents a surface that resembles pure gold and can be used as a "pure gold" surface for contact printing.

MYLAR® film modified with a sputter-deposited nickel/alloy topcoat was obtained from Courtaulds Performance Films (21034 Osborne Street, Canoga Park, CA 91304). Patterns of hydrophilic, carboxy-terminated alkane thiols were stamped onto the Ni/Au metallized MYLAR® using CH₃(CH₂)₁₅SH and HOC(O)(CH₂)₁₄SH acid by the following method. (See Figure 1). An exposed and developed photoresist pattern of 10 micron diameter circles on a silicon wafer was used as the master. Polydimethylsiloxane (PDMS; silicone elastomer 184; Dow Corning Co., Midland, MI), was polymerized on a master to produce a stamp with ten micron-diameter circles spaced five microns apart. The stamp was inked by exposure to a solution (1 to 10 mM

in ethanol) of 16-mercaptohexadecanoic acid, and allowed to air-dry. The substrate was contacted with the stamp for 50 seconds and washed for 2 to 4 seconds with a solution of hexadecanethiol (1 to 10 mM in ethanol). The substrate was finally washed for 10 seconds in ethanol and dried in a stream of nitrogen. The results of this printing are shown in Figure 2.

These hydrophilic self-assembling monolayer circles allow for selective placement of high surface tension fluids such as water, triethylene glycol, or ultraviolet light curable urethane acrylic adhesives. These liquids can contain dissolved and suspended reagents that react chemically or physically with targeted analytes, thus making the coated plastic film a collection of 10 micron microreactors suitable for low-cost, disposable chemical sensors. An example of such a device is shown in Figure 3a.

Diffraction of visible light was shown with these compositions. Both reflected and transmitted diffraction patterns were observed when using 5mW, 670 nm laser illumination. Figure 3b is a photograph of the diffraction pattern formed by visible light shown through the self-assembling monolayer pattern of Figure 3a. Rainbow diffraction colors were observed with transmitted white light.

Measurement of Contact Angles

Contact angles were measured on a Rame-Hart Model 100 goniometer at room temperature and ambient humidity. Water for contact angles was deionized and distilled in a glass and Teflon apparatus. Advancing and receding contact angles were measured on both sides of at least three drops of each liquid per slide; data in the figures represents the average of these measurements. The following method was used for measuring contact angles: A drop approximately 1-2 microliters in volume was grown on the end of a pipette tip (Micro-Electrapette syringe; Matrix Technologies; Lowell, MA). The tip was then lowered to the surface until the drop came in contact with the surface. The drop was advanced by slowly increasing the volume of the drop (rate approximately 1 microliter/second). Advancing contact angles of water were measured immediately after the front of the drop had smoothly moved a short distance across the surface. Receding angles were taken after the drop had smoothly retreated across the surface by decreasing the volume of the drop.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were collected on a Surface Science SSX-100 spectrometer using a monochromatized Al K-alpha source ($h\nu=1486.6$ electron volts). The spectra were recorded using a spot size of 600 micrometers and a pass energy on the detector of 50 electron volts (acquisition time for one scan was approximately 1.5 minutes). For the monolayers, spectra were collected for carbon and oxygen using the 1s peaks at 285 and 530 eV, respectively; the binding energies for elements in the monolayer were referenced to the peak due to hydrocarbon in the C 1s region, for which we fixed the binding energy at 284.6 eV. Spectra for the solid hydroxamic acid were collected using an electron flood gun of 4.5 eV to dissipate charge in the sample. The binding energies for the substrates were not standardized to a reference sample. All spectra were fitted using an 80% Gaussian/20% Lorentzian peak shape and a Shirley background subtraction. See J.P. Folkers, G.M. Whitesides, *et al.*, *Langmuir*, vol. 11, no. 3, pp. 813-824 (1995).

Condensation Figures

Condensation figures (CFs) are arrays of liquid drops that form upon condensation of vapor onto a solid surface. The examination of condensation figures has historically been used as a method to characterize the degree of contamination on an otherwise homogeneous surface. One is able to impose a pattern on arrays of condensed drops by patterning the surface underlying them into regions of different solid-vapor interfacial free energy and to characterize the patterned CFs by photomicroscopy and optical diffraction. It can be demonstrated that appropriately patterned CFs can be used as optical diffraction gratings and that examination of the diffraction patterns provides both a rapid, nondestructive method for characterizing patterned self-assembling monolayers and an approach to sensing the environment. Because the form of the CFs—that is, the size, density, and distribution of the drops is sensitive to environmental factors, CFs of appropriate size and pattern diffract light and can be used as sensors. This principle is demonstrated by correlating the temperature of a substrate patterned into hydrophobic and hydrophilic regions, in an atmosphere of constant relative humidity, with the intensity of light diffracted from CFs on these regions.

Appropriate patterns are formed from self-assembled monolayers (self-assembling monolayers) on gold/nickel by using combinations of hexadecanethiol $[\text{CH}_3(\text{CH}_2)_{15}\text{SH}]$, 16-mercaptohexadecanoic acid $[\text{HS}(\text{CH}_2)_{14}\text{COOH}]$, and 11-mercaptoundecanol $[\text{HS}(\text{CH}_2)_{10}\text{OH}]$. Several techniques are now available for preparing patterns of two or more self-assembling monolayers having 0.1- to 10- μm dimensions.

At 20°C, an incident beam of light from a laser (helium-neon laser, wavelength = 632.8 nm) produced a single transmitted spot because no water had condensed on the surface, and the transmittance of the regions covered with different self-assembling monolayers were effectively indistinguishable. As the surface was exposed to warm, moist air, droplets of water condensed preferentially on the hydrophilic regions. Diffraction patterns appeared in the light transmitted from the surface. Under these conditions, light was transmitted coherently from the regions where no water had condensed and was scattered by the regions where water had condensed. The condensation figures disappeared within several seconds as the water droplets which condensed on the self-assembling monolayers evaporated.

The ability to form condensation figures can be ascertained by the relative contact angles of water on the hydrophobic and hydrophilic self-assembling monolayers. Unpatterned monolayers of the appropriate thiol were prepared by immersion of the substrate in a dilute solution for one hour, followed by rinsing with ethanol and air drying.

The contact angles of water on Au(Ni)/MYLAR reacted with $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and $\text{HOC}(\text{O})(\text{CH}_2)_{14}\text{SH}$ were 100° and 62°, respectively. The untreated Au(Ni)/MYLAR contact angle for water was 73-77°. This water contact angle is similar to that obtained for Au coated SiO_x wafers, which is 73-74° (data not shown).

Condensation Figures [*Science*, Vol. 263, 60 (1994), incorporated herein by reference] with equivalent optical diffraction can be formed on Au/Ni:MYLAR®, relative to known art with Au:SiOx. The chemistry of alkane-thiols reacting with Au/Ni:MYLAR is similar to that reported in the literature for Au:SiOx.

A field emission secondary electron microscope image of 10 micron-diameter circles of hydrophilic self-assembling monolayers formed by printing of 16-mercaptohexadecanoic acid onto MYLAR® metallized with Ni/Au alloy is shown in Figure 2. Figure 3a is an optical photomicrograph at 300x magnification of 10 micron-

diameter circles of hydrophilic self-assembling monolayers formed by printing of 16-mercaptohexadecanoic acid, and after exposure to a high surface energy, curable, optical adhesive. The adhesive was cured by ultraviolet light (UV) exposure.

Figure 3b is a photograph of the diffraction pattern formed by visible light shown through the self-assembling monolayer pattern described by Figure 3a.

Figures 4a and 4b are field emission secondary electron micrograph images of 10 micron-diameter circles formed of self-assembled photocurable polymers on hydrophilic self-assembling monolayers.

Those skilled in the art will now see that certain modifications can be made to the invention herein disclosed with respect to the illustrated embodiments, without departing from the spirit of the instant invention. And while the invention has been described above with respect to the preferred embodiments, it will be understood that the invention is adapted to numerous rearrangements, modifications, and alterations, all such arrangements, modifications, and alterations are intended to be within the scope of the appended claims.

Claims

What is claimed is:

1. A film with patterned self-assembling monolayers thereon comprising:
a polymer film coated with a metal alloy; and
a self-assembling monolayer printed onto the polymer film.
2. The film of Claim 1, wherein the metals to be alloyed are selected from the group consisting essentially of gold, silver, nickel, platinum, aluminum, iron, copper, and zirconium.
3. The film of Claim 1, wherein the alloy coating is between approximately 1 nanometer and 1000 nanometers in thickness.
4. The film of Claim 1, wherein the polymer film is polyethylene-terephthalate, acrylonitrile-butadiene-styrene, acrylonitrile-methyl acrylate copolymer, cellophane, cellulosic polymers such as ethyl cellulose, cellulose acetate, cellulose acetate butyrate, cellulose propionate, cellulose triacetate, cellulose triacetate, polyethylene, polyethylene - vinyl acetate copolymers, ionomers (ethylene polymers) polyethylene-nylon copolymers, polypropylene, methyl pentene polymers, polyvinyl fluoride, and aromatic polysulfones.
5. The film of Claim 4, wherein the polymer film is polyethylene-terephthalate.
6. The film of Claim 1, wherein the polymer film is optically transparent.
7. The film of Claim 1, wherein the polymer film has an optical transparency between 5% and 95%.

8. The film of Claim 1, wherein the polymer film has an optical transparency between approximately 20% and 80%.

9. The film of Claim 1, wherein the self-assembling monolayer is formed from compounds with the following general formula:



wherein:

X is reactive with the metal or metal oxide on the polymer film;

R is a hydrocarbon chain; and

Y is a compound with any property of interest.

10. The film of Claim 9, wherein:

X is a asymmetrical or symmetrical disulfide (-R'SSR, -RSSR), sulfide (-R'SR, -RSR), diselenide (-R'Se-SeR), selenide (R'SeR, -RSeR), thiol (-SH), nitrile (-CN), isonitrile, nitro (-NO₂), selenol (-SeH), trivalent phosphorous compounds, isothiocyanate, xanthate, thiocarbamate, phosphine, thioacid or dithioacid, carboxylic acids, hydroxylic acids, and hydroxamic acids;

R and R' are hydrocarbon chains which may optionally be interrupted by hetero atoms, and which may optionally be perfluorinated, and which are preferably non-branched; and

Y is optionally hydroxy, carboxyl, amino, aldehyde, hydrazide, carbonyl, epoxy, or vinyl groups.

11. The film of Claim 9, wherein R is greater than 7 carbon atoms in length.

12. The film of Claim 9, wherein R is a compound of the form (CH₂)_a-Z-(CH₂)_b, wherein a²0, b²7, and Z is any chemical functionality of interest.

13. The film of Claim 12, wherein Z is selected from the group consisting of sulfones, lactams, and urea.

14. The film of Claim 1, wherein there are two or more self-assembling monolayers with different chemical properties.

15. The film of Claim 1, wherein a first self-assembling monolayer is hydrophobic, and a second self-assembling monolayer is hydrophilic.

16. A method of making a film with a self-assembling monolayer pattern comprising stamping a pattern of self-assembling monolayers on a polymer film coated with a metal alloy.

17. The method of Claim 16, wherein the metals to be alloyed are selected from the group consisting essentially of gold, silver, nickel, platinum, aluminum, iron, copper, and zirconium.

18. The method of Claim 17, wherein the metal alloy coating is between approximately 1 nanometer and 1000 nanometers in thickness.

19. The method of Claim 16, wherein the alloy is a nickel/gold alloy.

20. The method of Claim 16, wherein the polymer film is polyethylene-terephthalate, acrylonitrile-butadiene-styrene, acrylonitrile-methyl acrylate copolymer, cellophane, cellulosic polymers such as ethyl cellulose, cellulose acetate, cellulose acetate butyrate, cellulose propionate, cellulose triacetate, cellulose triacetate, polyethylene, polyethylene - vinyl acetate copolymers, ionomers (ethylene polymers) polyethylene-nylon copolymers, polypropylene, methyl pentene polymers, polyvinyl fluoride, and aromatic polysulfones.

21. The method of Claim 20, wherein the polymer film is polyethylene-terephthalate.

22. The method of Claim 16, wherein the polymer film is optically transparent.

23. The method of Claim 16, wherein the polymer film has an optical transparency between 5% and 95%.

24. The method of Claim 16, wherein the polymer film has an optical transparency between approximately 20% and 80%.

25. The method of Claim 16, wherein the self-assembling monolayer is formed from compounds with the following general formula:



wherein:

X is reactive with the metal or metal oxide on the polymer film;

R is a hydrocarbon chain; and

Y is a compound with any property of interest.

26. The method of Claim 25, wherein:

X is an asymmetrical or symmetrical disulfide (-R'SSR, -RSSR), sulfide (-R'SR, -RSR), diselenide (-R'Se-SeR), selenide (R'SeR, -RSeR), thiol (-SH), nitrile (-CN), isonitrile, nitro (-NO₂), selenol (-SeH), trivalent phosphorous compounds, isothiocyanate, xanthate, thiocarbamate, phosphine, thioacid or dithioacid, carboxylic acids, hydroxylic acids, and hydroxamic acids;

R and R' are hydrocarbon chains which may optionally be interrupted by hetero atoms, and which may optionally be perfluorinated, and which are preferably non-branched; and

Y is optionally hydroxy, carboxyl, amino, aldehyde, hydrazide, carbonyl, epoxy, or vinyl groups.

27. The method of Claim 25, wherein R is greater than 7 carbon atoms in length.

28. The method of Claim 25, wherein R is a compound of the form $(\text{CH}_2)_a\text{-Z-(CH}_2)_b$, wherein $a \geq 0$, $b \geq 7$, and Z is any chemical functionality of interest.

29. The method of Claim 28, wherein Z is selected from the group consisting of sulfones, lactams, and urea.

30. The method of Claim 16, wherein there are two or more self-assembling monolayers with different chemical properties.

31. The method of Claim 16, wherein a first self-assembling monolayer is hydrophobic, and a second self-assembling monolayer is hydrophilic.

32. The film of Claim 1, wherein the polymer is a thermoplastic polymer.

33. The method of Claim 16 wherein the polymer film is a thermoplastic polymer film.

34. The film of Claim 1, wherein the metal alloy is selected from the group consisting of Ni/Au, Pt/Au, and Cu/Au.

35. The method of Claim 16, wherein the metal alloy is selected from the group consisting of Ni/Au, Pt/Au, and Cu/Au.

36. A film with patterned self-assembling monolayers thereon comprising:
a polymer film coated with a metal alloy; and
a self-assembling monolayer printed onto the polymer film;

wherein the metal alloy has surface enrichment of a metal reacting with the self-assembling monolayer.

37. The film of Claim 36 wherein the metal alloy is selected from the group consisting of Ni/Au, Pt/Au, and Cu/Au.

38. A method of making a film with a self-assembling monolayer pattern comprising stamping a pattern of self-assembling monolayers on a polymer film coated with a metal alloy, wherein the metal alloy has surface enrichment of a metal reacting with the self-assembling monolayer.

39. The method of Claim 38 wherein the metal alloy is selected from the group consisting of Ni/Au, Pt/Au, and Cu/Au.

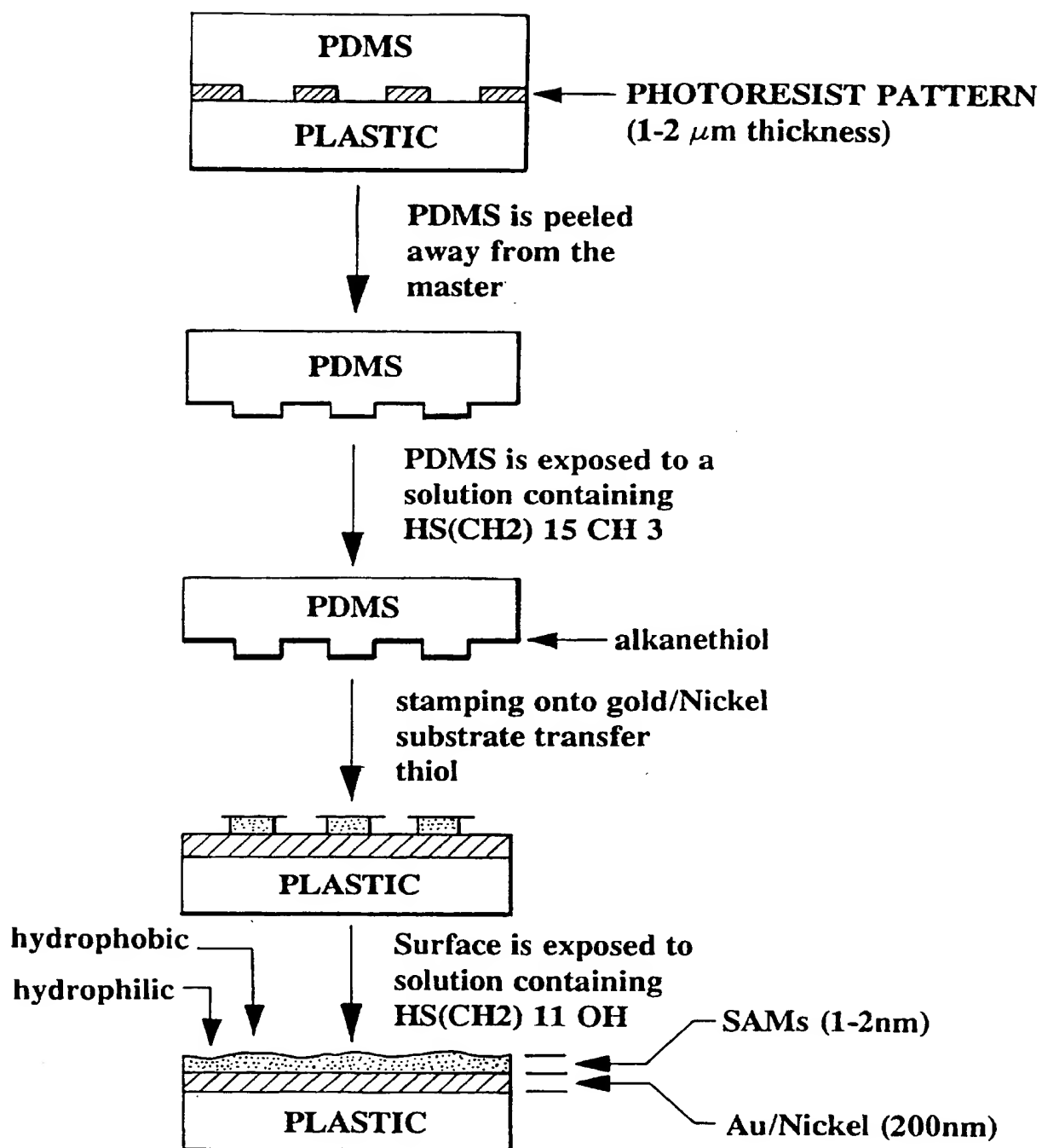


Fig. 1

2/5

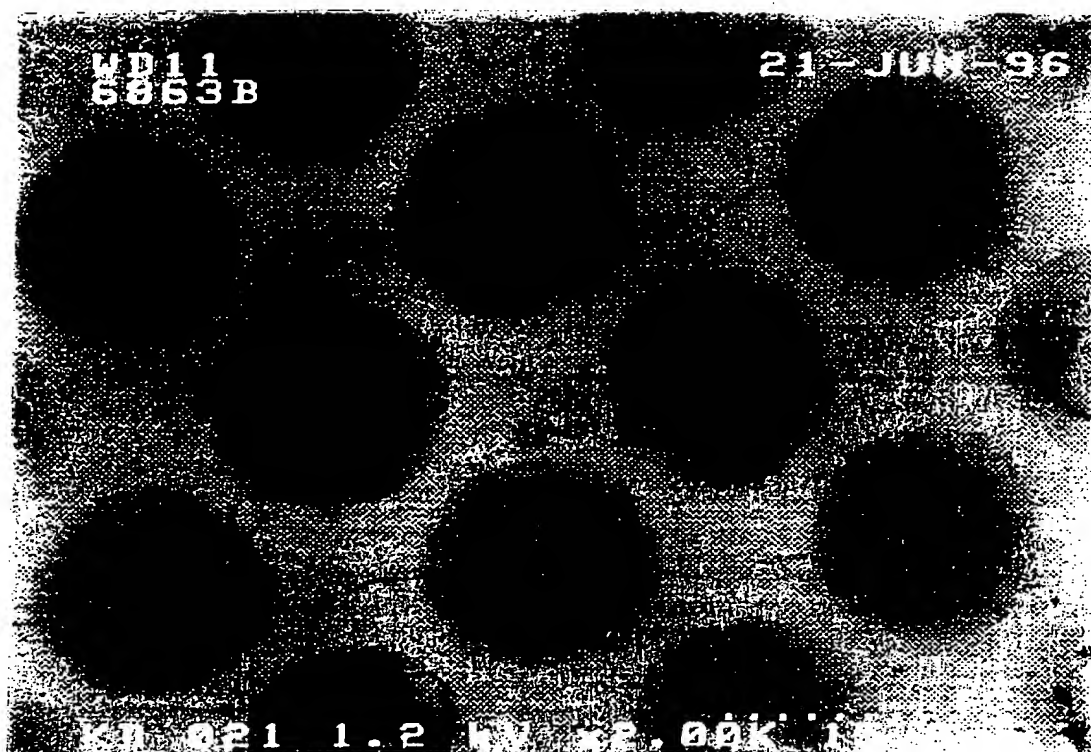


Fig. 2a

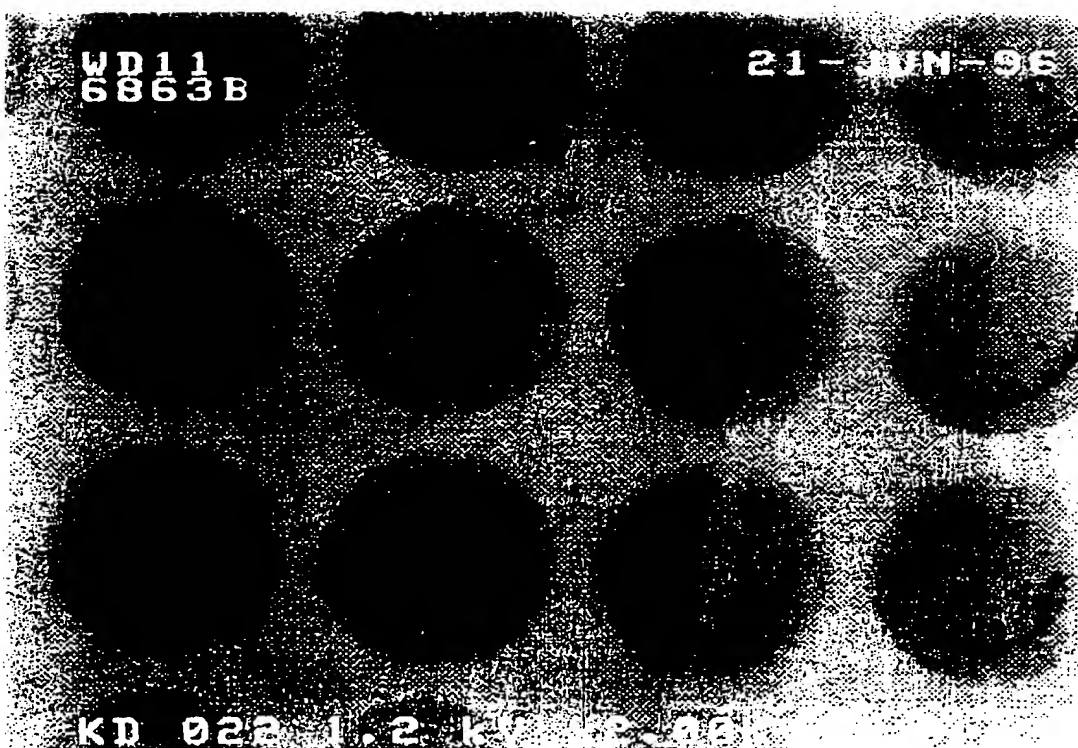


Fig. 2b

3/5

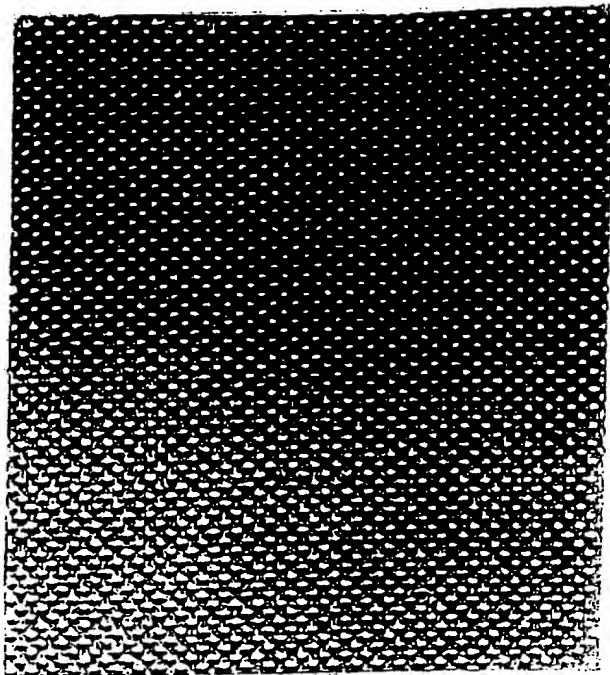


Fig. 3a

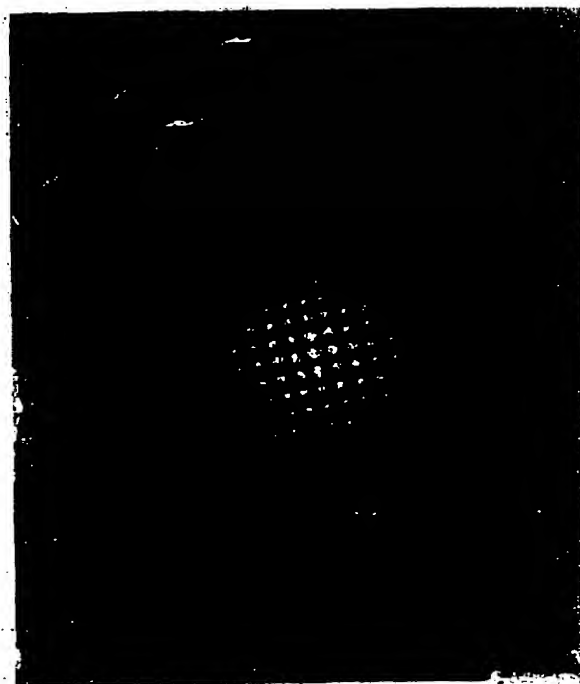


Fig. 3b

SUBSTITUTE SHEET (RULE 26)

BEST AVAILABLE COPY



Fig. 4a

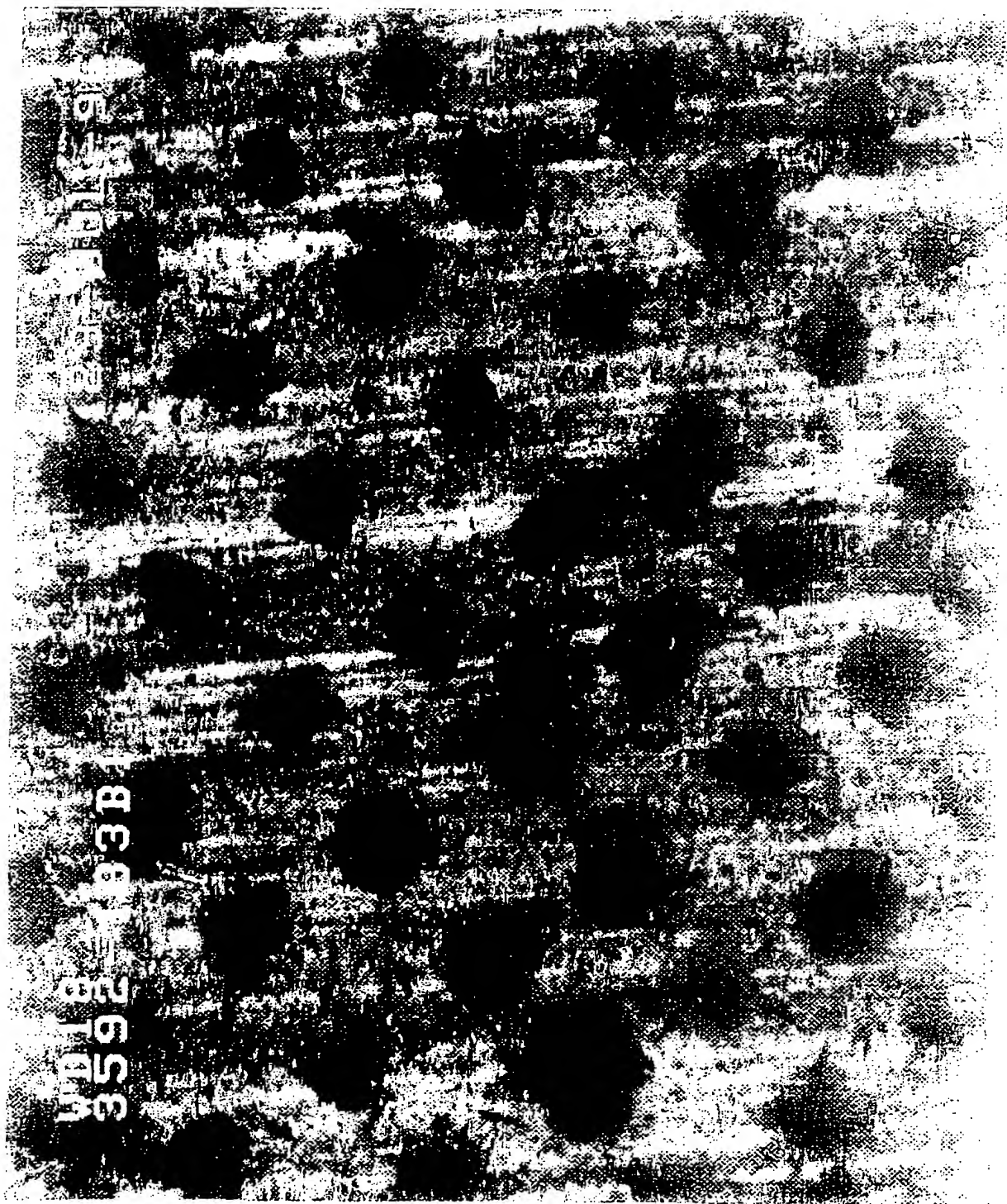


Fig. 4b

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 97/15566

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/00 B41M3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 512 131 A (KUMAR ET AL.) 30 April 1996 see column 5, line 62 - column 6, line 26 see column 10, line 29 - column 11, line 63 see column 12, line 25 - line 53 see column 14, line 41 - line 67 see column 19, line 50 - column 20, line 19; figure 1A -----	1-39

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

17 November 1997

Date of mailing of the international search report

28/11/1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Magrizos, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/15566

Patent document
cited in search report

Publication
date

Patent family
member(s)

Publication
date

US 5512131 A

30-04-96

NONE